Closed-pored silicone foams, process for producing them and their use

The present invention relates to closed-pored, elastic silicone foams obtainable by reacting addition-crosslinking silicone rubber mixtures with finely divided
5   ammonium hydrogen carbonate, a process for producing them and their use.

Silicone foam materials have been known for some time for various application areas using various production methods. The many application areas include thermal insulation at relatively high temperatures, the production of flexible seals, use as
10   damping elements in the form of foams, etc. These applications utilize the known properties of elastic silicone compositions: thermal stability, the small change in the mechanical properties at changing temperatures, the good ageing stability, etc.

The various methods of producing silicone foams are numerous and are utilized
15   depending on the specific requirements.

Widespread use is made of silicone compositions containing silicon-hydrogen groups which eliminate hydrogen during the crosslinking process. They can be reacted with silanol groups, alcohols or water. The hydrogen formed serves as blowing agent and
20   generates the silicone foam having the desired pore structure, cf., for example, EP-A 416 229. A further process is used in the production of silicone foam from high temperature vulcanizing, peroxidically crosslinkable siloxane compositions. Here, substances which decompose on heating serve as blowing agents which, at the moment of curing, produce the foamed siloxane composition. This process has found
25   wide application in industry and is described, for example, in US-A 2 857 343.

Furthermore, processes in which the gas-solubility, for example in moisture-curing silicone compositions, particularly at elevated pressure, is exploited have also been described. On releasing the pressure, the solubility drops suddenly and the gas
30   bubbles formed generate the desired silicone foam which is then crosslinked, for example by the action of water from atmospheric humidity, cf., for example, US-A 4 229 548.

A group of silicone compositions which are becoming ever more important are liquid
35   silicones or liquid silicone rubbers (LSRs). In comparison with other silicone compositions, they offer processing advantages in the production of rubber articles and thus open up new technological opportunities. LSR compositions are platinum-

catalysed, addition-crosslinking silicone mixtures which are efficiently processed in injection-moulding machines to produce shaped articles. The flowable, self-levelling silicone mixtures are likewise used as coatings for textiles where they are then crosslinked by action of heat.

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In the case of the LSR compositions too, there is a need to develop foamable mixtures. Thus, there is a need for three-dimensionally shaped foam articles. There has hitherto been no industrially satisfactory solution to the production of such articles since previously only foam sheets from which shaped articles had to be stamped have been produced. This method of production is time-consuming and at the same time associated with high material losses (scrap). An inexpensive production method which additionally allows three-dimensional shaping would therefore be the production of the shaped silicone foam article by injection moulding. This aim has not been able to be achieved because the decomposition temperature of blowing agents used does not match the curing temperature required for crosslinking. It is here necessary for the two temperatures to be close together so that foaming due to the decomposition of the blowing agent is hindered by parallel occurrence of crosslinking. This is, for example, made very clear in the use of sodium hydrogen carbonate as blowing agent for producing a shaped silicone foam article from an LSR product by means of injection moulding. Here, it is only possible to obtain shaped articles which contain only few gas bubbles, so that the quality requirements for a silicone foam are in no way fulfilled.

Similar problems are encountered when using LSRs in the production of textiles and fabrics coated with silicone foam. Here, complete foaming before crosslinking is likewise required. Blowing agents used hitherto produced only foams having a very low foaming factor since commencement of crosslinking did not allow optimum foaming. Here too, there is a need for a suitable mixture. In addition, there is the further important requirement for flame resistance of the silicone foam, since fabrics coated with silicone foam are frequently used in areas where fire is a threat. This need is in no way fulfilled by the sodium hydrogen carbonate described in EP-A 751 173. Although sodium hydrogen carbonate is also used as an intumescent substance in bulk silicone rubbers since a thermal insulation effect occurs due to foaming under the action of heat, cf. DE-A 3 713 267 and US-A 3 634 136, sodium hydrogen carbonate in the silicone foam itself causes a disadvantageous increase in the combustibility.

There is therefore a need for a blowing agent which releases blowing gas at a comparatively low temperature and simultaneously meets the requirement for flame-resistant silicone foams.
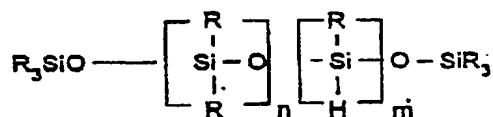
5 It is therefore an object of the present invention to provide closed-pored silicone compositions which can be foamed with an unproblematical blowing agent, do not have the disadvantages of the prior art and can be processed on injection moulding machines to produce shaped foam articles.

10 It has now surprisingly been found that this object can be achieved by reacting addition-crosslinking silicone compositions with a blowing agent containing finely divided ammonium hydrogen carbonate. These mixtures can be processed on injection moulding machines and additionally have a high flame resistance.

15 The present invention accordingly provides closed-pored silicone foams obtainable from the reaction of a mixture of

a)   100 parts by weight of at least one vinyl-containing, linear or branched organopolysiloxane containing at least 2 vinyl groups and having a viscosity 20   of from 0.1 to 1000 Pa·s,

b)   from 3 to 200, preferably from 5 to 50, parts by weight of at least one, optionally surface-modified, filler,

25 c)   from 0.5 to 10, preferably from 1 to 8, parts by weight of hydrogensiloxane having at least 3 SiH functions per molecule,

d)   from 0.01 to 10, preferably from 0.03 to 5, ppm of platinum in the form of a platinum catalyst,

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e)   from 0.01 to 5, preferably from 0.03 to 3, parts by weight of an inhibitor and

f)   from 0.3 to 10 parts by weight of finely divided ammonium hydrogen carbonate having a mean particle size of less than 40 μm as blowing agent,

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which are foamed and cured at temperatures above 60°C.

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The vinyl-containing organopolysiloxanes (a) are preferably linear or branched organopolysiloxanes containing at least two vinyl groups, whose viscosity measured using a rotation viscometer at 20°C can be in the range from 0.1 to 1000 Pa·s. Particular preference is given to vinyl-terminated polydimethylsiloxanes having a

5   viscosity of from 0.2 to 150 Pa·s, if desired in admixture with polydimethylsiloxanes containing lateral vinyl groups.

All viscosities indicated were determined at 20°C in accordance with DIN 53 019.

10   Examples of fillers (b) are extenders such as quartz and cristobalite flour and also precipitated or pyrogenic silicas, whose surface is preferably treated before or during the mixing process with substances known per se, e.g. silazanes with and without addition of water.

15   Component b) is preferably finely divided, pyrogenic or precipitated silica which may, if desired, be surface-modified with hexamethyldisilazane and/or tetramethyldivinyldisilazane.

Component (c) for the purposes of the invention is known polyorganosiloxanes

20   which bear hydrogen atoms on at least three silicon atoms, e.g. compounds of the formula

$$R_3SiO \longrightarrow \left[\begin{array}{c} R \\ | \\ Si-O \\ | \\ R \end{array} \right]_n \left[\begin{array}{c} R \\ | \\ -Si- \\ | \\ H \end{array} \right]_m O - SiR_3$$

25   where   R = C_1-C_8-alkyl, C_6-C_8-aryl,

m ≥ 3 and

m+n =   3-1000, and the units -$SiOR_2$ and -$SiRHO$ are randomly distributed in the molecule.

30   The Pt catalyst (d) is preferably Pt complexes which catalyse the addition of Si-H groups onto vinylsiloxanes. Preference is therefore given to Pt(0) complexes having vinylsiloxanes as ligands. However, it is also possible to use other metal complexes such as Rh compounds. Preference is given to using Pt(0) complexes which have vinylsiloxane ligands and are soluble in the siloxane polymers.

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Suitable inhibitors (e) are all compounds which make possible a controlled reduction of the crosslinking rate, but do not cause irreversible damage to the catalyst.

Particular preference is given to short-chain or cyclic polydimethylsiloxanes having a plurality of adjacent vinyl groups on the silicon atoms, e.g. tetramethyl-divinyldisiloxane and/or tetramethyltetravinylcyclotetrasiloxane.

The mean particle size of component f), which is determined by means of an optical microscope using a calibrated scale for counting and calculating the mean, is preferably less than 20 μm.

The amount of the blowing agent $(NH_4)HCO_3$ added is selected according to the desired degree of foaming. Preference is given to using from 0.3 to 5 parts.

In addition, it is possible to use further additives such as pigments or additives for increasing the flame resistance, e.g. carbon black or TiO_2.

The present invention also provides a process for producing the closed-pored silicone foams of the invention, wherein the components a) to f) are mixed at a temperature of ≤ 50°C, applied to a substrate by means of a doctor blade and foamed and simultaneously cured in hot air at temperatures above 60°C, preferably from 100 to 200°C. Alternatively, the mixture can also be cured at the same temperatures in a partly filled mould, e.g. using an automatic injection-moulding machine, to give a moulded foam.

The invention further provides for the production of moulded foam, wherein the components a) to c) and, if desired, f) are mixed, injected into moulds by means of injection moulding and foamed and cured there at temperatures above 60°C.

The present invention additionally provides for the use of the foams of the invention on textiles, also with incorporation of woven wire meshes, as upholstery materials and as thermal insulation and fire protection materials.

The following examples, in which all parts are parts by weight, illustrate the invention but do not restrict it.

Examples

Example 1   (comparison)

5   In a dissolver, the base mixture was prepared by mixing 5.0 kg of vinyl-terminated polydimethylsiloxane (polymer type a) having a viscosity at 20°C of 10 Pa·s and 9.0 kg of vinyl-terminated polydimethylsiloxane having a viscosity at 20°C of 65 Pa·s with 1.35 kg of hexamethyldisilazane and 0.47 kg of water and subsequently mixed with 6 kg of pyrogenic silica having a BET surface area of 300 m^2/g

10   (measured by N_2 adsorption) to give a homogeneous mixture (incorporation of the filler as described in the German layed-open publication 2 535 334). The mixture was first heated to 130°C and stirred for 1.5 hours in a closed dissolver and then freed of water and other volatile constituents at 160°C in a vacuum. After cooling, this base mixture was mixed with 4.0 kg of polymer type a and 0.0033 kg of a

15   tetramethyltetravinylcyclotetrasiloxane containing 15% of Pt in the form of a Pt complex (corresponds to 10 ppm of Pt in the total formulation) having tetramethyltetravinylcyclotetrasiloxane as ligand to produce the A component.

To prepare the B component, a base mixture was prepared from the same amounts as

20   above, but was mixed with 3.5 kg of polymer type a, 0.04 kg of ethinylcyclohexanol and 0.75 kg of a trimethylsilyl-terminated polymethylhydrogensiloxane having, on average, 20 methylhydrogensiloxy units and 20 dimethylsiloxy units per molecule.

100 g of each of the two components A and B were taken and intensively mixed

25   together with 4 g of finely divided sodium hydrogen carbonate.

The mean particle size of the $NaHCO_3$, which was determined by means of an optical microscope using a calibrated scale by counting and calculating the mean, was 15 μm.

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A 1 mm thick layer of the mixture was applied to an aluminium foil by means of a doctor blade and foamed and cured for 5 minutes at a temperature of 180°C in a convection drying oven. 5 strips having dimensions of 12.7 mm × 150 mm were cut from the about 2.5 mm thick foam sheet and used for a laboratory burning test based

35   on DIN 54 336. For this purpose, a butane gas burner flame was applied for 15 seconds to the bottom end of the strips and the afterflame time and afterglow time were measured.

The mean afterflame time determined from the 5 specimens was 129 seconds, with three specimens even burning down over their entire length. For all specimens, the afterflame time was characterized not only by afterglowing but additionally by a sometimes crackling flame.

Example 2   (according to the invention)

100 g of the A and B components prepared in Example 1 were likewise taken and intensively mixed together with 4 g of ammonium hydrogen carbonate. The mean particle size of the NH_4HCO_3, which was determined by means of an optical microscope using a calibrated scale by counting and calculating the mean, was 15 μm. A 1 mm thick layer of the mixture was applied to an aluminium foil by means of a doctor blade and foamed and cured for 5 minutes at a temperature of 180°C in a convection drying oven.

As in Example 1, 5 strips having dimensions of 12.7 mm × 150 mm were cut from the about 5 mm thick foam sheet and subjected to the same laboratory burning test mentioned above. Here, the average afterglow time was only 34 seconds. In addition, it may be noted that

-        a weak flame was observed for only a few seconds after removing the burner flame and only weak glowing then occurred,
-        crackling burning did not occur and
-        none of the samples burned down over their entire length.

This example thus demonstrated improved flame resistance when using NH_4HCO_3 instead of $NaHCO_3$.

Example 3   (comparison)

In a dissolver, the base mixture was prepared by mixing 15.2 kg of vinyl-terminated polydimethylsiloxane (polymer type a) having a viscosity of 10 Pa·s with 2 kg hexamethyldisilazane, 0.13 kg of tetramethyldivinyldisilazane and 0.8 kg of water and subsequently mixed with 7.6 kg of pyrogenic silica having a BET surface area of 300 m²/g to give a homogeneous mixture (incorporation of the filler described in the German layed-open publication 2 535 334). The mixture was first heated to 130°C

and stirred for 1.5 hours in a closed dissolver and then freed of water and other volatile constituents at 160°C in a vacuum. After cooling, this base mixture was mixed with 19.1 kg of polymer type a, 1.43 kg of tetramethyltetravinylcyclo-tetrasiloxane and a further 0.0109 kg of tetramethyltetravinylcyclotetrasiloxane
5   containing 1500 ppm of Pt in the form of a Pt complex (corresponds to 0.184 ppm of Pt in the total formulation) having tetramethyltetravinylcyclotetrasiloxane as ligand to produce the A component. 0.69 kg of a finely divided sodium hydrogen carbonate was mixed in. The mean particle size, which was determined by means of an optical microscope using a calibrated scale by counting and calculating the mean, was
10   10 μm.

To prepare the B component, a base mixture was prepared from the same amounts as above and was now mixed with 15.1 kg of polymer type a, 5.07 kg of a trimethylsilyl-terminated polymethylhydrogensiloxane having, on average, 20
15   methylhydrogensiloxy units and 20 dimethylsiloxy units per molecule and likewise with 0.65 kg of the abovementioned sodium hydrogen carbonate.

The two components were mixed in an injection-moulding machine (from Arburg) and injected into a shortened sheet mould having the dimensions: length 175, width
20   115 and thickness 2 mm and 6 mm (divided into two), with the following conditions giving the best result:

Injection time:	2.8-36 sec
Temperature:	180-185°C
Curing time:	70 sec

Despite the optimization experiments carried out, even the best setting gave only very unsatisfactory foam formation. This was the case even when 2500 ppm of the inhibitor ethinylcyclohexanol were added. At temperatures below 180°C, no foam
30   formation was observed, while at higher temperatures of about 180°C crosslinking occurred too rapidly despite the added inhibitor so that the decomposition of the blowing agent can no longer effect foam formation. The sheet therefore appeared too glassy with too few gas bubbles.

Example 4   (according to the invention)

Use was made of the two components A and B prepared as in Example 1, but a batch comprising 40% of ammonium hydrogen carbonate (particle size 15 μm, measured as in Example 2) and 60% of a vinyl-terminated polydimethylsiloxane of type a (viscosity 10 Pa·s) was additionally mixed at a temperature below 50°C into the component A in such an amount that the concentration of ammonium hydrogen carbonate was 4%. As a result, the mixture formed in the injection moulding machine (Arburg) from the two components contained 2 per cent of ammonium hydrogen carbonate. This mixture was injected into a heated sheet mould having the dimensions: length 175 mm, width 115 mm and thickness 2 mm and 6 mm (divided in two) under the following conditions:

Injection time:	3-115 sec
Temperature:	150-160°C
Curing time:	70-90 s

Under these conditions, a foam sheet having a homogeneous foam structure was obtained. The foam density was about 0.6 g/cm^3. In optimization experiments, it was found that the addition of the inhibitor ethinylcyclohexanol in the range of about 1000-3000 ppm had a favourable effect. In any case, the desired homogeneous foam structure was achieved at the relatively low mould temperature of 150-160°C.